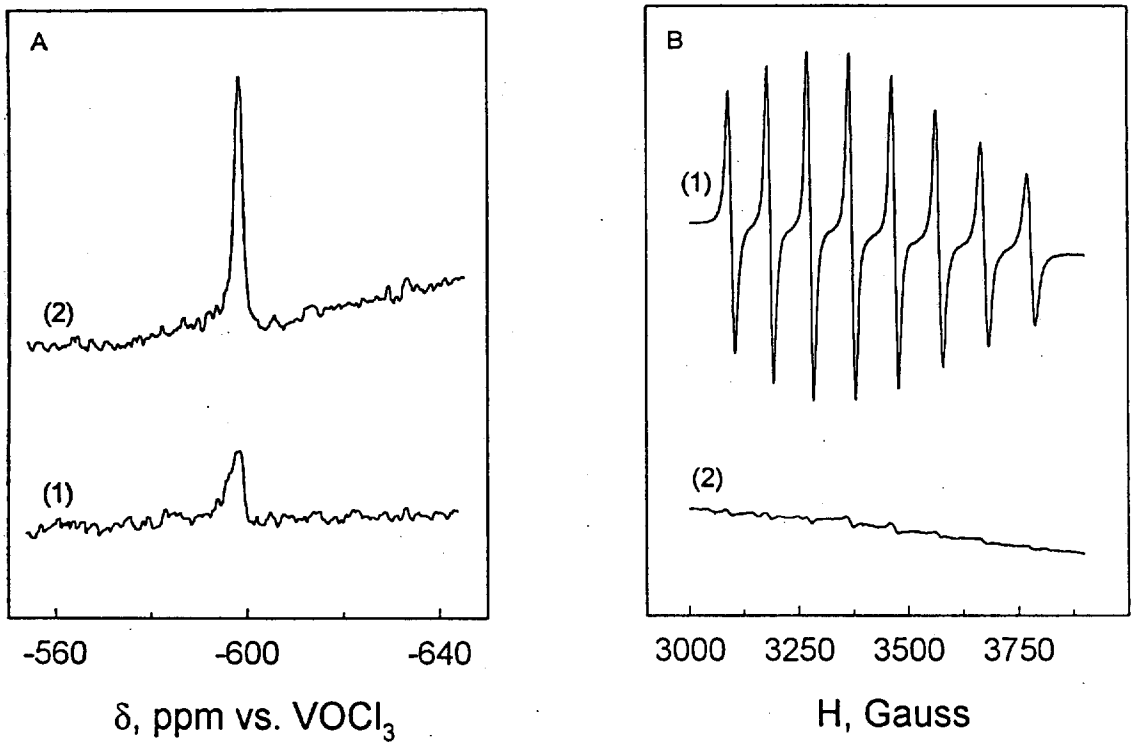

Figure S1. (A) ^{51}V NMR spectra of: (1) The solution resulting when 2 millimoles/liter of CF_3SO_3H were added to a 2 mM solution of $V^{IV}O$(salen) in CH_3CN; (2) After O_2 was bubbled for 30 min. through a solution containing 2 mM $V^{III}(salen)^+$.

(B) (1) EPR spectrum of 2 mM $V^{IV}O$(salen) in CH_3CN; (2) After addition of 2 millimoles/liter of CF_3SO_3H to the solution in (1).

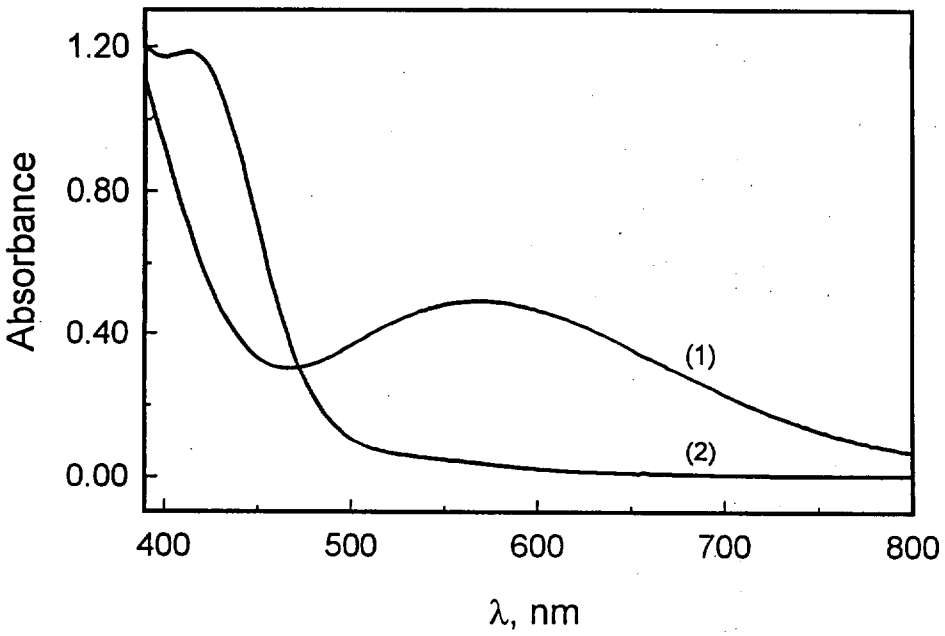

Figure S2. UV-vis spectra of (1) $V^{V}O(salen)^{+}$ and (2) $V^{III}(salen)^{+}$ in CH_3CN. Concentration of complex: 0.4 mM. Optical path length: 1 cm.

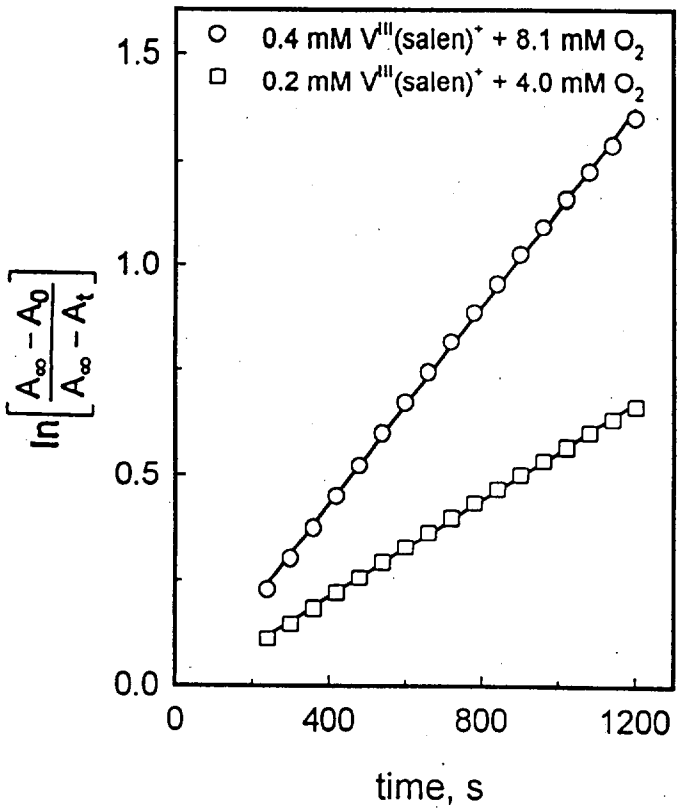

Figure S3. Pseudo-first-order kinetic plots for the reaction between $V^{III}(salen)^+$ and excess O_2 as monitored spectrophotometrically at 570 nm. A_0 = initial absorbance; A_t = absorbance at time t; $A\infty$ = absorbance after the completion of the reaction.